

Appendix EE
Assessing the Importance of Carbonyl Compounds
in Ozone Formation in Houston-Galveston:
Relative Reactivities of Carbonyl and Hydrocarbon Species

J. Jolly
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Summary

This paper examines the relative reactivities of two VOC classes, carbonyls and hydrocarbons, in the formation of ozone in the air in Houston-Galveston (HGA). This was accomplished by comparing reactivities for the two compound classes at sites, dates, and times where both classes were measured. This paper also looked at the relative importance of individual carbonyl species in ozone formation in the area.

Available carbonyl data are a tiny fraction of hydrocarbon data. Nonetheless some conclusions could be drawn from the comparison. First, carbonyl compounds were found to frequently be an important part of total (where “total” was defined as the sum of hydrocarbon and carbonyl) airmass reactivity for samples of low or moderate overall reactivity, but very rarely were they an important part of total reactivity when only the most reactive samples were analyzed. Next, carbonyl species, especially at Deer Park and Clinton monitors, seem to be an important part of total reactivity from certain wind directions, but these are directions where overall reactivity is less than some other directions. Finally, formaldehyde, and to a lesser extent acetaldehyde, were found to be much more important than all the other carbonyl species in ozone formation in Houston, by virtue of their high concentrations combined with their high reactivities.

Introduction

Both the TCEQ and outside entities have documented the importance of highly reactive volatile organic compounds (VOCs) in the rapid and robust ozone formation that occurs in HGA.^{1,2} Much of this work has clarified the role that reactive alkenes, especially ethylene and propylene, play in this phenomenon; less studied is the importance of carbonyl compounds, such as formaldehyde and acetaldehyde, in rapid ozone formation.

This study attempted to systematically assess the relative importance of carbonyl and hydrocarbon species in ozone formation by comparing measurements taken during the same time periods at the same sites, and calculating reactivities, by sample, for each of the two compound classes. Additionally, this study analyzed which carbonyl species, by virtue of their concentrations in the air and their potential to react to form ozone, were most important in rapid ozone formation in HGA.

Monitoring data from the TCEQ monitoring network were used for this study. Carbonyl

measurement data were available in SAS datasets from three separate sources at TCEQ: *carb1hr_through_q2_2002*, which contains one-hour samples from 1997-2002; *carb24hr_through_3_2002*, which contains 24-hr samples for the same years; and the *carbonyl_YYYY* datasets, which contain both 3- and 24-hr samples for intermittent periods from 1987-2001. For the *carbonyl_YYYY* datasets, it was decided to use only the data from 1995-2001, because data are available more regularly in that period. **Table 1** lists the total number of non-missing samples for each of these three averaging times, during the study period.

Table 1
Carbonyl Dataset Statistics

Carbonyl Dataset Statistics			
Averaging Period	Years	No. Species Measured	No. of Non-Missing Samples
1-hour	1997-2002	16	444
3-hour	1995-98	3	291
24-hour	1998-2002	18	562

Hydrocarbon measurements were taken using automated gas chromatographs (Auto-GCs) colocated with the carbonyl monitors. These measurements are taken hourly; they are 40-minute averages, but were treated as hourly measurements for matching with the carbonyl samples.

Carbonyl and colocated hydrocarbon data were available from six monitors in HGA: Aldine CAMS 8, Clinton CAMS 403, Deer Park CAMS 35, Channelview CAMS 15, HRM 3, and Bayland Park CAMS 53 (See **Figure 1** for map of monitors). Not all of the monitors had data for all of the carbonyl averaging periods, or for all of the years.

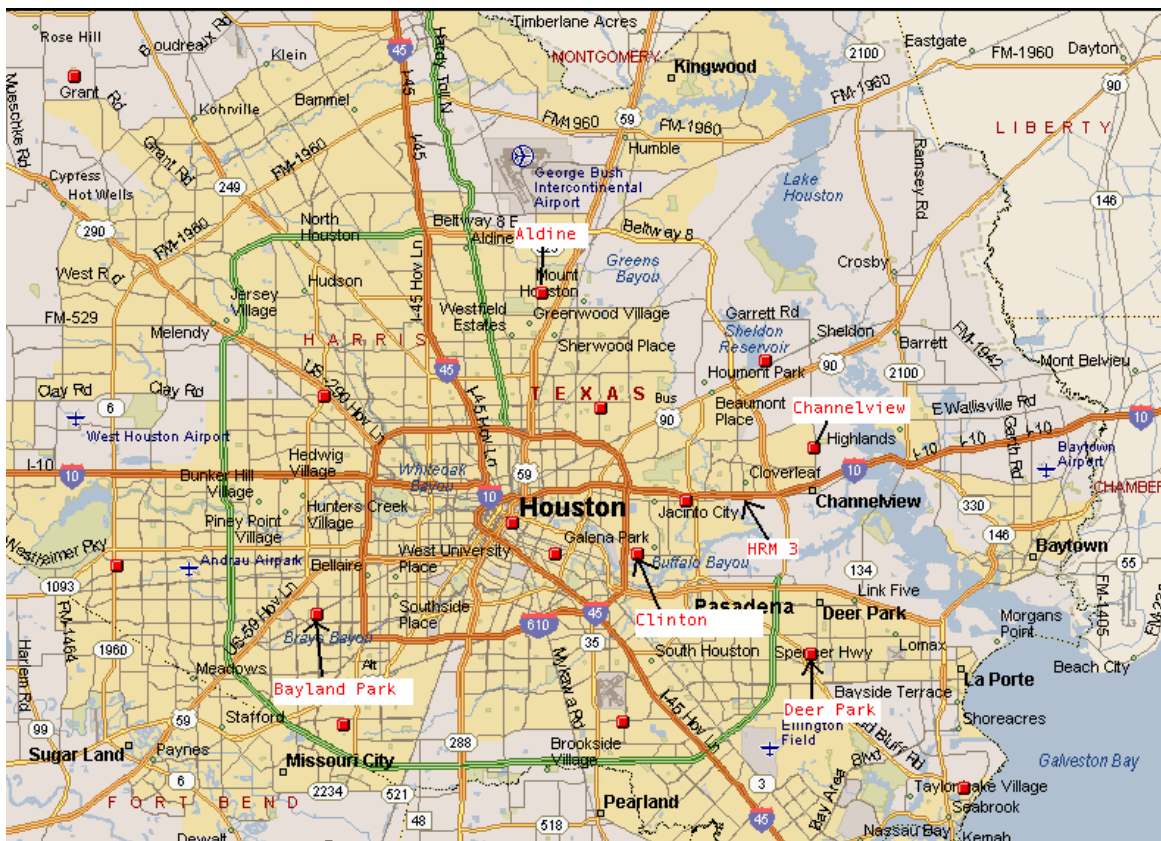


Figure 1 – Map of Study Monitors

This project was originally intended to assess individual and total carbonyl reactivity in the Beaumont-Pt Arthur (BPA) area as well. However, the only available Auto-GC (hydrocarbon) and carbonyl measurements in that area were taken at two different monitors. This made it difficult if not impossible to assess relative reactivities of the two compound classes; for this reason, no analysis was conducted in BPA.

Analyses were conducted using four different combinations of data: 1) merging one-hour carbonyl data with matching hydrocarbon data, 2) merging three-hour carbonyl data with matching hydrocarbon data, 3) aggregating one- and three-hour carbonyl data and merging it with matching hydrocarbon data, and 4) merging 24-hr carbonyl data with matching hydrocarbon data.

All of the reactivity analyses performed in this study were based on calculations using compound-specific Maximum Incremental Reactivity (MIR) values found in Column H of William P. L. Carter's *r02tab.xls*, available on his website.³ These values represent the maximum number of grams of ozone formed per gram of VOC, under ideal conditions. MIR conversion factors were created by multiplying each compound's MIR value times the ratio of the compound's molecular weight to the molecular weight of ozone. These factors were then multiplied times ambient VOC measurements – measured in units of parts per billion by volume (ppbv) – to give measurements of reactivity times concentration, described in this study simply as “MIR Reactivity.” For ambient measurements that were in units of parts per billion carbon

(ppbC) rather than ppbv, the factors were first divided by the number of carbon atoms in the particular VOC, before being multiplied times that compound's measured concentration to get MIR reactivity.

For analyses in which the reactivities of the two compound classes were compared, MIR reactivities calculated for each compound in a carbonyl sample were summed, and compared with the sum of reactivities from the corresponding hydrocarbon sample (i.e., for the same hour at the same monitor). This gave total carbonyl and hydrocarbon MIR reactivities for each sample.

Analysis/Results

I. Relative Reactivities of 2 Classes of VOCs: Hydrocarbons and Carbonyls

A. Reactivity Due to Carbonyls – All Wind Directions Combined

A.1. One-hour Carbonyl Data

Frequency distributions were created for each monitor showing the percent of total reactivity attributable to carbonyl species versus percent of total reactivity attributable to hydrocarbon species. These distributions combined all wind directions.

This analysis was done for all one-hour carbonyl samples which had concurrent Auto-GC samples, and for a subset of that set consisting of those samples whose aggregate hydrocarbon reactivity was at least 166, which is the 90th percentile of hydrocarbon reactivity of all airplane measurements taken during the TXAQS 2000 Study.⁴

When all samples were included, it was observed that carbonyl contribution to total reactivity varied widely for each monitor (see **Figures 2-6**). The range was 2.4% (Deer Park) to 95.7% (Bayland Park). (Some samples showing 100% of reactivity due to carbonyl compounds at Clinton are probably due to invalid Auto-GC measurements.) The median carbonyl contribution to total reactivity ranged from 40.9% (Clinton) to 65.5% (Channelview).

When only samples with hydrocarbon reactivity at least 166 were analyzed (**Figs. 7-10**), carbonyl contribution to total reactivity dropped substantially across all 4 monitors (Channelview did not have any samples meeting this criterion). Median percent reactivity due to carbonyls dropped between 20 and 32% at the monitors. The peak sample at any monitor was 64% at Clinton; the other 3 monitors together had only 2 samples above 40% reactivity due to carbonyls. (Note that in Figure II-I.A.1.7, the term “PAMS” in the title refers to hydrocarbon species; this nomenclature is used elsewhere in this paper.)

These results show that carbonyls often played a significant role in reactivity of less-reactive airmasses, but they almost always played a lesser role, relative to hydrocarbon species, in airmasses which were highly reactive due to hydrocarbons. **Figures 11-17**, which show hydrocarbon and carbonyl reactivities for all samples for each monitor, further illustrate this.

A.2. Three-hour Carbonyl Data

Distributions similar to those prepared in Section A.1 were prepared using the three-hour carbonyl data. As with the one-hour data, they were prepared by merging the samples with concurrent Auto-GC samples for each monitor. The only difference was that 3 Auto-GC samples were merged with each three-hour carbonyl sample. If less than three hours of Auto-GC data were available, the hours lacking hydrocarbon data were dropped from the comparison. The distributions were prepared for Clinton and Deer Park, as three-hour data were only available from these two monitors.

The distribution of percent reactivity due to carbonyl compounds in the three-hour samples at Clinton, for all available hours (**Figure 18**), shows that median percent reactivity was 21.4%. This was about half of what was seen at that monitor when all one-hour samples were used. When only samples with hydrocarbon reactivity at least 166 were included (**Figure 19**), median percent reactivity due to carbonyls was just 11.6%, as compared to 21% when the same criterion was applied to Clinton one-hour samples.

At Deer Park, when all common hours were compared (**Figure 20**), median percent reactivity due to carbonyls was 32.6%, as compared to 49.4% with the one-hour data. When only samples with hydrocarbon reactivity at least 166 were used (**Figure 21**), median percent reactivity was 12.3%, as compared to 20.0% for the one-hour data.

There are several things which could explain the uniform reduction in median percent reactivity due to carbonyls when 3-hr data are substituted for one-hour data. First, overall hydrocarbon reactivity may be higher during the former sample times, as compared to the latter. This would cause carbonyl contribution to total reactivity to be smaller. It's also possible that the air arrived from different directions during the two sample groups; if it passed over different source regions, that could affect proportion of reactivity due to the two compound classes.

Another variable which could help explain the difference is time of sample; the three-hour samples were largely collected in the late evening and to a lesser extent in mid- to late-afternoon (**Figure 22**); the one-hour samples were mostly collected in the morning or early afternoon (**Figure 23**). It is possible that carbonyl concentrations peak during daytime, due to their formation from the reaction of olefins and the hydroxyl (OH) radical. If so, then the late-evening-oriented three-hour samples might be expected to show relatively smaller contribution to total reactivity than would the daytime one-hour samples. It would seem fairly simple to compare mean diurnal reactivities of these two compound classes, to gain insight into relative reactivities by hour of day; perhaps special study data, such as that gathered at Williams Tower or La Porte Airport during TXAQS 2000, might provide carbonyl data for each hour of the day. Although time limitations prevented this from being done, it is hoped that this question can be answered in future work on this topic.

A.3. 24-hr Carbonyl Data

As with the one- and three-hour carbonyl samples, distributions of percent reactivity due to

carbonyl compounds were prepared using the 24-hr carbonyl samples. These were prepared by merging each 24-hr sample with 24 corresponding one-hour Auto-GC samples. If less than 24 hours of Auto-GC data were available, the hours lacking hydrocarbon data were dropped from the comparison. Six monitors had 24-hr data, and thus had distributions prepared: Clinton, Deer Park, Bayland Park, Channelview, HRM 3, and Aldine.

As with the other data, distributions were prepared for two different criteria: 1) all hours having both carbonyl and hydrocarbon data, and 2) only those hours whose Auto-GC samples had reactivity of at least 166. When all samples were used (**Figures 24-30**), percent reactivity due to carbonyls ranged from 0.7% (Clinton) to 92.4% (Deer Park). Median percent reactivity due to carbonyls ranged from 17.2% (HRM 3) to 34.3% (Bayland Park).

When only hours with hydrocarbon reactivity at least 166 were used (**Figures 31-36**), median percent reactivity due to carbonyls dropped at every monitor. The decreases ranged from 7.0% (HRM 3) to 24.1% (Bayland Park). The decreases in median percent reactivity due to carbonyls, when the high hydrocarbon reactivity subset is substituted for the entire set, are consistent with the one- and three-hour data.

B. Reactivity by Wind Direction

B.1. Reactivities Using one-hour Carbonyl Data

Scatter plots were created showing hydrocarbon and carbonyl MIR reactivities for each concurrent set of one-hour samples. These show reactivities by one-hour average resultant wind direction (in compass degrees) for the sample hour at the monitor.

Channelview (**Figure 37**) did not have enough data to form meaningful conclusions. The plot for Bayland Park (**Figure 38**) shows that for some wind directions, carbonyl reactivity was a significant part of overall reactivity, but not for wind directions 0-90, where the most reactive air came from. This monitor also showed gaps in data from particular directions, including 180-225 and 290-330.

At Clinton (**Figure 39**), between wind directions 180 and 315, carbonyl reactivities appeared to be roughly equivalent to hydrocarbon reactivities. Overall reactivity appeared lowest from those directions. The highest carbonyl reactivities occurred between wind directions 90 and 135, where there were even higher hydrocarbon reactivities.

At Deer Park (**Figure 40**), extremely high hydrocarbon reactivities near wind directions 45 and 315 had the effect of suppressing the other data on the plot, making conclusions difficult.

No wind direction analysis was conducted for the HRM 3 monitor whatsoever in this study. This is because the monitor had a relatively small number of samples, and its meteorological data were not available in SAS datasets, but rather in another file format, which would have required conversion. Given the limited time available to do this study, it was decided not to study this monitor.

The data presented in the scatter plots were used to calculate geometric mean of MIR reactivity

by wind direction, using 45-degree wind bins. This was calculated for Deer Park, Clinton, and Bayland Park (not enough data were available for Channelview). Hours with low wind speeds (less than 2 miles/hour) were removed, due to concerns about the representativeness of wind direction readings at such wind speeds.

The geometric mean plots show that at Clinton (**Figure 41**), mean carbonyl reactivities are higher at bins 90 through 225 than in the other bins, but only at bin 225 was carbonyl reactivity higher than hydrocarbon reactivity. At Deer Park (**Figure 42**), carbonyl reactivities exceeded hydrocarbon reactivities at bins 180 and 225, and were roughly equal at bins 90, 135, and 270, but were considerably less at the northwest, north, and northeast bins. At Bayland Park (**Figure 43**), the highest hydrocarbon reactivities were at bins 45 and 90; carbonyl reactivities were highest at those bins and at 270. However, at this monitor, the number of data points used to calculate geometric mean for each bin was quite low; there were no data for bin 315.

B.2. Reactivities Using One-hour Carbonyl Data Normalized for Wind Speed

A simple Gaussian Dispersion Model (for plume centerline concentration) can be represented as follows:⁵

$$\chi \equiv \frac{Q}{2\pi u \sigma_y \sigma_z} \quad (\text{II-1})$$

Where χ = concentration, Q = emission rate, u = wind speed, and σ_y and σ_z are lateral and vertical dispersion coefficient functions, respectively.

This equation indicates that the concentration of a pollutant observed at a location is proportional to the emission rate(s) of upwind source(s), and inversely proportional to wind speed and to the degree of lateral and vertical dispersion (this model does not account for any loss of the pollutant due to reaction or deposition). One of the purposes of looking at observed concentrations by wind direction – as we are doing in this study – is to understand which upwind regions contain sources of highly reactive emissions.

This equation shows that observed concentrations increase as wind speed decreases. We can gain a clearer picture of upwind emissions sources by filtering out the effect of wind speed on observed concentration – that is, by normalizing for wind speed. If equation II-1 above is simplified by removing the effects of lateral and vertical dispersion on concentration, we get the following equation:

$$\chi \equiv \frac{Q}{u} \quad (\text{II-2})$$

If both sides of this equation are multiplied times u , we see that normalized concentration is equal to observed concentration times wind speed. Another way of looking at this is saying that elevated concentrations can be due not only to high upwind emissions, but to low wind speeds. By normalizing for windspeed, we correct those concentrations which are high only because windspeeds are low.

To further clarify upwind source regions, we could normalize the concentration data for atmospheric stability as well. The values for σ_y and σ_z are proportional to the degree of solar radiation; the samples used in this study were probably collected over a range of solar intensities, which would have an effect on the degree of dispersion of upwind pollution. This normalization was not undertaken in this study, however, due to time and resource limitations.

In scatter plots like those presented in this paper, normalizing for windspeed can have the effect of rearranging the peaks to better show which directions are downwind from sources or regions of reactive emissions. For the mean values calculated in this paper, normalizing can again show which directions are downwind from reactive source regions. It is important to note that normalizing does not change the proportion of a single sample's reactivity due to hydrocarbons versus carbonyls.

Results of Normalized One-hour Data

Bayland Park did not have many one-hour carbonyl samples; the scatter plot showing its normalized reactivities (**Figure 44**) does not show significant differences from the non-normalized data. At Clinton, however, normalizing for windspeed clarifies the directions associated with highly reactive airmasses (**Figure 45**). One can see here that wind directions 150-180 were clearly the directions most associated with very high reactivity, and that this high reactivity is due largely to hydrocarbons. One can also see a cluster of relatively high carbonyl reactivities between directions 90-130.

The scatter plot of normalized reactivity values at Deer Park (**Figure 46**) shows very high hydrocarbon reactivities around 40 and 330 degrees, and somewhat elevated reactivities (of both compound classes) between 90 and 180.

B.3. Reactivities Using One- and Three-hour Carbonyl Data – Normalized and Non-normalized

For this analysis, one- and three-hour carbonyl data were aggregated and then merged with

concurrent one-hour Auto GC and wind speed and direction data, for Clinton and Deer Park (there were no three-hour data for Bayland Park or Channelview). The decreased resolution inherent in a longer averaging time—as with the three-hour samples here—is undesirable for a study, such as this one, which seeks to identify geographical source areas. However, given the relatively limited one-hour data set (see table), we decided to use the three-hour data to increase the sample size.

Scatter plots were prepared showing these data both non-normalized and normalized. At Clinton, the non-normalized data show (**Figure 47**) that there are relatively high hydrocarbon reactivities in airmasses coming from all directions except approximately 210-300 degrees. When these data are normalized (**Figure 48**), one can see that air coming from about 150-190 degrees was much more reactive than was air from other directions, and air coming from directions 210-50 degrees (proceeding clockwise) was never highly reactive.

At Deer Park, the non-normalized data (**Figure 49**) showed that very reactive airmasses always came from either 30-40 degrees, or 315-320 degrees. The normalized data show these (**Figure 50**) same two peaks, demonstrating that they are not due to low windspeeds. The normalized data also show that air coming from about 110-140 degrees often had elevated reactivity (though not as high as the first two peaks) due to both carbonyls and hydrocarbons.

Geometric mean of normalized MIR reactivity was calculated for Clinton and Deer Park using the data shown in the scatter plots. These means were calculated for 30-degree wind direction bins. These are smaller than the 45-degree bins used earlier; the smaller size was used because of the increased number of data points. Another difference from the geometric means calculated earlier is that whereas hours with low wind speeds were omitted from the earlier analysis, they were included in the current one. They were included here because by virtue of the data being normalized, their importance is decreased.

Figure 51 shows geometric means at Clinton by 30-degree bin. Here, it can be seen that the highest hydrocarbon reactivities were at bins 90-180 (East through South), and the highest carbonyl reactivities were at bins 120-180. For these four bins, hydrocarbon reactivity ranged from 1.6 times greater than carbonyl reactivity (bin 120) to 5.6 times greater than carbonyl reactivity (bin 90). Conversely, at bin 240, carbonyl reactivity was about 25% greater than hydrocarbon reactivity. However, mean total reactivity of air coming from this direction was much lower than from bins 90-180.

Two graphs were prepared for Deer Park. This was because the scaling of the first one (**Figure 52**) is stretched to accommodate an extremely high mean reactivity at bin 300; not only does this make viewing of the other data difficult, but the bin 300 mean was derived from just one hydrocarbon (and its corresponding carbonyl) sample. In the second graph (**Figure 53**), data for bin 300 have been removed. In this graph it can be seen that from bins 90-270 (proceeding clockwise), carbonyl reactivity was a significant part of total reactivity; it ranged from 38 to 56% of total reactivity for these bins. However, by far the highest mean total reactivity (outside of bin 300) was seen at bin 30; there, carbonyl reactivity only accounted for 20% of that figure.

B.4. Reactivities Using 24-hr Carbonyl Data

The same directional analyses performed using the one- and three-hour carbonyl data were done for the 24-hr carbonyl data. In addition to the four monitors used for the prior analyses, Aldine CAMS 8 was used as well.

For this analysis, each 24-hr sample was merged with 24 concurrent one-hour Auto-GC samples, along with concurrent hourly meteorological data. Hours missing either Auto-GC or meteorological data were dropped. Geometric means using 45-degree wind direction bins were calculated for the five monitors.

24-hour carbonyl samples are more abundant than their one- or three-hour counterparts, in the TCEQ database. Unfortunately, there are not enough of them to overcome the loss of resolution when a single sample is merged with 24 different hourly wind direction measurements. **Figure 54** shows four scatter plots -- from left to right, Clinton carbonyl and hydrocarbon reactivities, and the same two for Deer Park, by wind direction. The lack of directional resolution in the carbonyl samples, especially as compared to their one-hour hydrocarbon counterparts, is very clear. Whereas the hydrocarbon plots suggest upwind source regions, no such inference can be made from the carbonyl samples.

The graphs comparing mean reactivity of the two compound classes at Clinton (**Figure 55**) and Deer Park (**Figure 56**), by wind bin, unsurprisingly did not reveal much variation in reactivity by wind direction for the carbonyl data. This is in contrast to the normalized 1- and 3-hour means calculated in Section B.3. Bayland Park (**Figure 57**) shows a somewhat higher carbonyl mean reactivity at bin 45. Channelview (**Figure 58**) shows essentially no directional variation, whereas Aldine (**Figure 59**) shows a higher mean carbonyl reactivity when winds are from the Southeast.

II. Analyses of Individual Carbonyl Compounds

A. Normalized Species Concentrations by Wind Direction

In order to understand which wind directions tend to be associated with elevated concentrations of individual carbonyl species, scatter plots showing normalized species concentrations were prepared for Clinton (**App. II-A1**) and Deer Park (**App. II-A2**). They were prepared using the one-hour carbonyl data. Concentrations were normalized by multiplying them times the hourly resultant wind speed.

One can see that at both monitors, certain compounds have “peaks” which may indicate source regions. At Clinton, there are several species that have high normalized concentrations near 180 degrees – benzaldehyde, butylaldehyde, and crotonaldehyde. Acetaldehyde and formaldehyde both show some high concentrations between about 90 and 130 degrees; both appear to have more elevated concentrations between about 80 and 210 degrees than all other directions. Acetone shows a peak at 180 degrees, but elevated concentrations (normalized at 50 ppb or greater) were seen in winds from a variety of different directions. Propanal showed elevated concentrations between about 60 and 200 degrees. MEK_methacrolein showed almost no directional association. The remaining compounds had nearly all, or all, of their normalized

concentrations less than or equal to 1 ppbv, making them unimportant.

At Deer Park, there appeared to be less directional association than at Clinton. Acetaldehyde was observed in lower concentrations between 150 and 270 than from other directions. Acetone, conversely, was measured in higher (normalized) concentrations from these directions than from others. Neither Benzaldehyde, butylaldehyde, nor crotonaldehyde showed clear directional association. Formaldehyde appeared to show its highest normalized concentrations between about 90 and 180 degrees, except for two very high values near 30-40 degrees. MEK_methacrolein, as at Clinton, showed high values from a number of directions. The remaining species' normalized concentrations were nearly all below 1 ppbv.

It can be difficult to deduce much from these scatter plots, because of the limited availability of data. In general it appears that many of the species at both monitors have apparent peaks at or near the same directions that highly reactive hydrocarbon peaks have been shown to occur at. Also, peaks are often seen between about 90 and 180 degrees, which, especially in the case of Deer Park, may be because of secondary formation of these species from ozone formation reactions, and arrival of compounds due to afternoon winds, which are often from those directions. Finally, one can see that formaldehyde, acetaldehyde, and acetone were found to have much higher normalized concentrations than the other species.

B. Composition of Carbonyl Reactivity, by Monitor and Wind Direction

Geometric means of reactivity of individual carbonyl species were calculated, by 30-degree wind bins, for Deer Park and Clinton, using one-hour carbonyl data. For each bin, each species' reactivity was aggregated to see which species were important when the wind came from a particular direction.

Figure 60 shows these results for Clinton. One can see that formaldehyde and acetaldehyde were, as far as their contribution to carbonyl reactivity, the most and second-most important species, respectively, no matter which direction the wind came from. Formaldehyde composed from 43.6 to 56.9% percent of total reactivity. Acetaldehyde often had a total reactivity greater than that of all other species. The other species accounted for from 16.4% (bin 120) to 33.5% (bin 240) of total carbonyl reactivity.

At Deer Park (**Figure 61**), formaldehyde and acetaldehyde also were observed to be the two most important species, as with Clinton. Formaldehyde provided from 43.7 to 60.3% of total reactivity. But at bin 240, acetone composed a greater part of total reactivity than did acetaldehyde – the only case where a species other than acetaldehyde was the second most important species.

The overall large contribution of acetone to total normalized carbonyl concentration does not translate into this species playing an important role in total carbonyl reactivity. That's because it is so unreactive (its MIR is less than one-twentieth that of formaldehyde) that, overall, it is relatively unimportant for ozone formation.

Summary / Next Steps

This study compared overall carbonyl reactivity to hydrocarbon reactivity, as well as looking at relative reactivity of individual carbonyl species observed in HGA. Total reactivity was defined in this study as the sum of carbonyl and hydrocarbon reactivity. While these two classes comprise many important compounds in ozone formation, there are other classes, such as ethers, amines, acetates, and chlorinated organic compounds, which may contribute to ozone formation but which were not assessed here.

Another obstacle in this study was the relative paucity of carbonyl data. At the six study monitors, during the study's duration, over 110,000 hourly hydrocarbon samples were measured; this compares with about 1300 carbonyl samples.

In spite of these limitations, this study revealed some important things. It was seen that carbonyl contribution to total reactivity was usually minor when very reactive airmasses were measured, but it was often a significant part of airmasses which had low or moderate total reactivity. High carbonyl reactivities appeared to be associated with certain wind directions at some monitors. This suggests either upwind emissions sources, or upwind reaction of alkenes in ozone formation, which results in formaldehyde and other carbonyls. Finally, this study found that at Deer Park and Clinton, formaldehyde and acetaldehyde were the two most important species, as far as contribution to total carbonyl reactivity, from nearly every wind direction.

There are several fairly clear next steps which could shed additional light on the role of carbonyls in overall reactivity in Houston. The carbonyl data are of course very limited, but data permitting, analyses could be done on carbonyl contribution to total reactivity by time of day, day of week, and by season. This could help answer the question of when are carbonyls more and less important for ozone formation in Houston. It could also be useful to plot locations of point sources of formaldehyde and acetaldehyde, to explore the correlation between these emissions and concentrations of the two species at study monitors. Even though some carbonyls are formed secondarily rather than emitted, such an analysis might reveal that these species are underreported in the emission inventory, as are some of the reactive hydrocarbons.

It would also be useful to analyze monitoring data from outside the TCEQ network. There are data from the LaPorte and Williams Tower sites, collected by outside researchers during TXAQs 2000. These data were obtained when this project was close to finishing.

References

1. Ryerson, T. B., et al, Effect of petrochemical industrial emissions of reactive alkenes and NO_x on tropospheric ozone formation in Houston, Texas, *J. Geophys. Res.*, 108, No. D8, 8-1 - 8-24, 2003
2. Texas Commission on Environmental Quality, Revisions to the State Implementation Plan

(SIP) for the Control of Air Pollution, Technical Support Document, December 13, 2002.
<http://www.tnrcc.state.tx.us/oprd/sips/tsdpart3.pdf>

3. Carter, W. P. L., the Saprc-99 Chemical Mechanism and Updated Voc Reactivity Scales, Revised 2/5/2003, <http://pah.cert.ucr.edu/~carter/reactdat.htm#data>

4. Texas Commission on Environmental Quality, Revisions to the State Implementation Plan (SIP) for the Control of Air Pollution, Technical Support Document, Attachment 5, December 13, 2002.
ftp://ftp.tnrcc.state.tx.us/pub/OEPAA/TAD/Modeling/HGAQSE/Modeling/Doc/TSD_PHASE1/attachment5-airborne_canister.pdf

5. "Gaussian Dispersion Model," <http://www.csun.edu/~vchsc006/469/gauss.htm>